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RAMAN EFFECT IN RELATION TO CRYSTAL STRUCTURE: SODIUM NITRATE

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(Communicated by Professor S. Bhagavantam, F.A.SC.)

1. *Introduction*

Very few systematic attempts have so far been made to explain the observed striking differences, in respect of the Raman and infra-red spectra, between a free ion and the crystal of which it forms a part. Bhagavantam and Venkatarayudu* have tackled this problem and indicated the general lines along which modifications are to be expected. According to these authors, the Raman spectrum of a crystal need not be identical with that obtained either in the molten or the dissolved states of the same substance although there may be similarities in several respects. Firstly, the values of the frequencies of particular oscillations may change on account of the existence of inter-ionic forces. Secondly, some of the lines may split into close components, the selection rules for the various components being entirely different among themselves and from those of the ion. Finally, some new lines may appear or some of those already existing in the ion may disappear in the crystal. This last result is of importance in connection with the origin of low-frequency Raman lines in crystals. Bhagavantam and Venkatarayudu have shown, in their paper already referred to, that the so-called lattice oscillations are simply the internal oscillations of the structure and that no special mechanism need be postulated for explaining their origin.

2. *The Case of Sodium Nitrate*

To illustrate these conclusions, the cases of sodium nitrate and calcite amongst other crystals, had been dealt with by them in a general manner.

The character table for the free NO_3 ion (Table I) shows that there should be two single (ν_1 and ν_2) and two doubly degenerate (ν_3 and ν_4) internal normal modes. ν_1 represents the total symmetric oscillation and is Raman active and infra-red inactive. ν_2 represents the mode in which the central

* *Proc. Ind. Acad. Sci.*, 1939, 9, 224.

TABLE I

Normal Modes of the Nitrate and Carbonate Ions

D_{3h}	E	$2C^1$	$3C_2$	σ_h	$2S^1$	$3\sigma_v$	n_i	R & T	n_i'	Raman	Infra-red
A_1' ..	1	1	1	1	1	1	1	..	1	p	f
A_2' ..	1	1	−1	1	1	−1	1	1	0	..	..
E_1' ..	2	−1	0	2	−1	0	3	1	2	D	$M_\perp \neq 0$
A_1'' ..	1	1	1	−1	−1	−1	0	..	0	..	..
A_2'' ..	1	1	−1	−1	−1	1	2	1	1	f	$M_z \neq 0$
E_2'' ..	2	−1	0	−2	1	0	1	1	0	..	..
U_R ..	4	1	2	4	1	2					
$h_j \cdot \chi_j'$ ..	12	0	−6	4	−4	6					
$h_j \cdot \psi_j'$ ..	6	0	0	4	−4	6					

atom moves along the trigonal axis and is Raman inactive and infra-red active. ν_3 and ν_4 are active in both Raman effect and infra-red absorption.

On the other hand, the character table for the $NaNO_3$ crystal (Table II) shows that there should be nine single and nine degenerate normal modes.

TABLE II

Normal Modes of the Sodium Nitrate and Calcite Structures

D_{3d}^6	E	$2S_6^1$	$2C^1$	i	$3\sigma_v$	$3C_2$	n_i	External T	External L	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	0	0	1	p	f
A_2 ..	1	1	1	1	−1	−1	3	0	2	1	f	f
B_1 ..	1	−1	1	−1	1	−1	4	1	2	1	f	p
B_2 ..	1	−1	1	−1	−1	1	2	0	1	1	f	f
E_1 ..	2	1	−1	−2	0	0	6	1	3	2	f	p
E_2 ..	2	−1	−1	2	0	0	4	0	2	2	p	f
U_R ..	10	2	4	2	0	4						
$h_j \cdot x_j'$ ..	30	0	0	−6	0	−12						

The Raman active and infra-red inactive total symmetric oscillation of the NO_3 ion splits into two modes, one of which comes under A_1 (Raman active and infra-red inactive) and the other under B_2 (inactive in both). The second non-degenerate mode of the free ion which is inactive in the Raman effect and active in the infra-red splits into two which come under A_2 (inactive in both) and B_1 (Raman inactive and infra-red active). The two doubly degenerate oscillations of the free ion, however, undergo a marked modification in the crystal. Both of these, in the case of the free ion, are active in the Raman effect as well as infra-red absorption. In the crystal, they continue to be degenerate but split into four modes and come under the representations E_1 and E_2 with altered selection rules. E_1 is active in the

infra-red but inactive in the Raman effect while E_2 is Raman active and infra-red inactive. As a consequence of this, we should expect absence of exact coincidence between the Raman and the infra-red frequencies in the $NaNO_3$ crystal, whereas in the case of the free ion, the Raman effect frequencies coincide exactly with those obtained from measurements in infra-red absorption.

In addition to the four doubly degenerate and four single frequencies accounted for above, we should also expect five doubly degenerate and five single frequencies entirely characteristic of the crystal and which may be termed the lattice oscillations.

That all these features are exhibited in the Raman and infra-red spectra of calcite and sodium nitrate has been pointed out before. It is intended in this paper to make a quantitative study of the changes that are to be expected in the exact frequencies of the free ion and of the actual values in respect of the new oscillations that arise in the sodium nitrate crystal by postulating suitable crystalline forces.

The force-constants relevant to the case of the free ion can be calculated from the frequencies observed in solution and with the help of the following set of equations.

$$\lambda_1 = \frac{k + 3K_1}{m}; \quad \lambda_2 = K_3 \cdot \frac{M + 3m}{3mM};$$

$$\lambda_3 + \lambda_4 = \frac{2M + 3m}{2mM}(K + 3K_2) + \frac{3K_1}{2m};$$

$$\lambda_3\lambda_4 = \frac{3(M + 3m)}{4m^2M} \times (KK_1 + 4KK_2 + 3K_1K_2).$$

The λ's are related to the corresponding ν's by the equation $\lambda^2 = 4\pi^2\nu^2$. Identifying ν_1, ν_2, ν_3, ν_4 with 1048, 830, 725 and 1361 respectively,* the following values are obtained.

$K = 5{\cdot}42 \times 10^5$, $K_1 = 1{\cdot}65 \times 10^5$, $K_2 = 0{\cdot}64 \times 10^5$ and $K_3 = 4{\cdot}40 \times 10^5$.

Here K and K_1 represent respectively the forces between nitrogen-oxygen and oxygen-oxygen atoms in the NO_3 ion. K_2 relates to a variation in the angle between any two N — O bonds and K_3 arises when the nitrogen atom moves out of the plane of oxygens.

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* These values have been obtained in sodium nitrate solution and are taken from Hibben, *Raman Effect and its Chemical Applications* (1939).

3. *Normal Co-ordinates and Normal Frequencies of the Sodium Nitrate Structure*

The normal co-ordinates in respect of the various representations have already been worked out by Bhagavantam and Venkatarayudu and given in an earlier paper already referred to. Some of these, which have been erroneously entered, have to be corrected as below:—

$$Q_2'(L) = (Z_3 - Z_4) + (Z_5 + Z_6 + Z_7 - Z_8 - Z_9 - Z_{10})$$

$$Q_3'(i) = 3m_3(Z_3 - Z_4) - m_2(Z_5 + Z_6 + Z_7 - Z_8 - Z_9 - Z_{10})$$

$$Q'_{17a}(L) = (x_3 - x_4) + (x_5 - x_8 + x_7 - x_{10} + x_6 - x_9)$$

$$Q'_{18a}(i) = 3m_3(x_3 - x_4) - m_2(x_5 + x_6 + x_7 - x_8 - x_9 - x_{10})$$

Q'_{17b} and Q'_{18b} are similar to Q'_{17a} and Q''_{18a} and must be corrected accordingly.

In order to calculate the frequencies in the case of the crystal, three additional force-constants have been introduced into the potential energy function.* These are:

K_4: force brought into play when the angle at any atom on the trigonal axis changes by one unit. This axis is a unique direction in the structure and in the static condition, all the atoms on it are collinear and hence every one of the angles is 180°.

K_5: force brought into play when the distance between a sodium and the nearest oxygen atoms changes by one unit.

K_6: force brought into play when a twist of one unit in the trigonal axis is produced by the bodily rotation of the individual NO_3 groups.

With the foregoing notation of force-constants, the frequencies coming under the various irreducible representations (Table II) can be written down as follows. Details of calculation are omitted.

In the following equations,

$$r = \frac{b^2}{4a^2 + b^2};\ s = \frac{ab}{4a^2 + b^2};\ t = \frac{a^2}{4a^2 + b^2}$$

a = distance between two nearest nitrogen and oxygen atoms

* It must be mentioned here that the choice of these is somewhat arbitrary. The actual state of affairs in a crystal is obviously much more complicated and these force constants and the values that will be ascribed to them in the course of the paper can at best be regarded as representing, in effect, the sum total of all the possible types of crystalline forces. The description given cannot be interpreted as literally corresponding to what exists in the crystal.

b = distance between two nearest nitrogen atoms.

$p = \mathrm{M} + 3m$

and $p_1 = \mathrm{M} + 3m + \mathrm{M}'$

M′, M and m are respectively the masses of sodium, nitrogen and oxygen atoms.

A_1: $\lambda = \dfrac{\mathrm{K} + 3\mathrm{K}_1 + 8t\,\mathrm{K}_5}{m}$

A_2: λ's are the roots of:

$$\begin{vmatrix} 12\,\mathrm{K}_5 r - 2p\lambda & -12\,\mathrm{K}_5 r\mathrm{M} & 0 \\ -12\mathrm{K}_5 r\mathrm{M} & 12\mathrm{K}_5 r\mathrm{M}^2 + 2\mathrm{K}_3 p^2 - 6m\mathrm{M}p\lambda & 0 \\ 0 & 0 & -24m\lambda \end{vmatrix} = 0$$

B_1: λ's are the roots of:

$$\begin{vmatrix} 16\mathrm{K}_6 - 24m\lambda & 0 & 0 \\ 0 & 12\mathrm{K}_5 r\mathrm{M}^2 + 2p^2\mathrm{K}_3 - 6m\mathrm{M}p\lambda & 12\mathrm{K}_5\mathrm{M}rp_1 \\ 0 & 12\mathrm{K}_5\mathrm{M}rp_1 & 12\mathrm{K}_5 p_1{}^2 r - 2\mathrm{M}'pp_1\lambda \end{vmatrix} = 0$$

B_2: λ's are the roots of:

$$\begin{vmatrix} \mathrm{K} + 3\mathrm{K}_1 + 8t\mathrm{K}_5 - m\lambda & 2s\mathrm{K}_5 \\ 48s\mathrm{K}_5 & 12r\mathrm{K}_5 - 2\,\mathrm{M}'\lambda \end{vmatrix} = 0$$

E_1: λ's are the roots of:

$$\begin{vmatrix} 24\mathrm{K}_5 r - 12m\lambda & -48s\mathrm{K}_5 & 24s\mathrm{K}_5 & 24\mathrm{M}s\mathrm{K}_5 & 24p_1 s\mathrm{K}_5 \\ -48s\mathrm{K}_5 & 12\mathrm{K} + 36\mathrm{K}_1 + 36\mathrm{K}_2 + 96\mathrm{K}_5 t - 24m\lambda & -48\mathrm{K}_5 t & -6p\mathrm{K} + 18p\mathrm{K}_2 - 48\,\mathrm{M}t\mathrm{K}_5 & -48p_1 t\mathrm{K}_5 \\ 24s\mathrm{K}_5 & -48t\mathrm{K}_5 & 24t\mathrm{K}_5 + 8\mathrm{K}_4 - 2\mathrm{M}^1\lambda & 24\mathrm{M}t\mathrm{K}_5 - 24m\mathrm{K}_4 & 24p_1 t\mathrm{K}_5 + 8p_1\mathrm{K}_4 \\ 24\mathrm{M}s\mathrm{K}_5 & -6p\mathrm{K} + 18p\mathrm{K}_2 - 48\mathrm{M}t\mathrm{K}_5 & 24\mathrm{M}t\mathrm{K}_5 - 24m\mathrm{K}_4 & 3p^2\mathrm{K} + 9p^2\mathrm{K}_2 + 24\mathrm{M}^2 t\mathrm{K}_5 + 144m^2\mathrm{K}_4 - 6m\mathrm{M}p\lambda & 24\mathrm{M}p_1 t\mathrm{K}_5 - 48mp_1\mathrm{K}_4 \\ 24p_1 s\mathrm{K}_5 & -48p_1 t\mathrm{K}_5 & 24p_1 t\mathrm{K}_5 + 8p_1\mathrm{K}_4 & 24\mathrm{M}p_1 t\mathrm{K}_5 - 48mp_1\mathrm{K}_4 & 24p_1{}^2 t\mathrm{K}_5 + 16p_1{}^2\mathrm{K}_4 - 2\mathrm{M}^1 pp_1\lambda \end{vmatrix} = 0$$

E_2: λ's are the roots of:

$$\begin{vmatrix} 12K + 36K_1 + 36K_2 + 96tK_5 - 24m\lambda & 48tK_5 & -6pK + 18pK_2 - 48MtK_5 & -48sK_5 \\ 48tK_5 & 24tK_5 + 8K_4 - 2p\lambda & -24MtK_5 + 24mK_4 & -24sK_5 \\ -6pK + 18pK_2 & -24MtK_5 & 3p^2K + 9p^2K_2 + 24M^2tK_5 + 72m^2K_4 - 6mMp\lambda & 24MsK_5 \\ -48MtK_5 & +24mK_4 & & \\ -48sK_5 & -24sK_5 & 24MsK_5 & 24K_5r - 12m\lambda \end{vmatrix} = 0$$

4. *Numerical Values of the Force-Constants and of the Frequencies in the Crystal*

The total number of force-constants introduced in the case of the crystal is thus seven. The numerical values assumed for them are:

$$K = 5{\cdot}42 \times 10^5;\ K_1 = 1{\cdot}78 \times 10^5;\ K_2 = 0{\cdot}64 \times 10^5;$$
$$K_3 = 4{\cdot}40 \times 10^5 \text{ and } K_4 = 0{\cdot}03 \times 10^5;\ K_5 = 0{\cdot}35 \times 10^5;$$
$$K_6 = 0{\cdot}07 \times 10^5.$$

K_1, K_2 and K_3 are the same as those calculated for the free ion. K_1 is here $1{\cdot}78 \times 10^5$ whereas it was $1{\cdot}65 \times 10^5$ in the free ion. This increase is effected as each oxygen atom in a crystal will be under the force-field of a large number of other oxygens whereas in the ion we need consider only the influence of its two nearest neighbours. The values of K_4, K_5 and K_6 have been chosen to give a reasonably good fit with the experimentally observed values of the crystalline frequencies.

Taking the above values of the force-constants, the frequencies that are attributed to the case of the $NaNO_3$ crystal can be evaluated. The actual values obtained under each representation along with the activity rule are given below.

A_1 (Raman active, infra-red inactive): 1069.

A_2 (Inactive in both): 840, 229, 0.

B_1 (Infra-red active, Raman inactive): 843, 439, 71.

B_2 (Inactive in both): 1069, 380.

E_1 (Infra-red active, Raman inactive): 1411, 716, 292, 157, 60.

E_2 (Raman active and infra-red inactive): 1362, 766, 190, 87.

The results thus obtained have been summarised and compared with the experimental observations in Table III.

TABLE III

Raman	Calc. ..	87,		190,		766,	1069,		1362
	Obs. ..	94,		185,		718,	1068,		1382
Infra-red*	Calc. ..	60,	71,	157,	292,	439,	716,	843,	1411
	Obs. ..	71,	71,	133,	217,	217,	692,	831,	1405

* The values of the observed infra-red frequencies are quoted from Schæfer and Matossi's book *Das Ultra Rote Spectrum*, 1930.

5. *Discussion of Results*

The following important conclusions can be drawn from the foregoing results.

The frequency of the total symmetric oscillation which is 1048 in the free ion should increase to 1069 in the crystal. This is confirmed by experiment.

The two doubly degenerate oscillations of the free ion remain doubly degenerate but split into four modes, two of which come under E_1 and two under E_2. E_1 is infra-red active but Raman inactive while E_2 is Raman active but infra-red inactive. Hence, there should be no exact coincidence between the observed Raman and infra-red frequencies and this is confirmed by experiment.

The Raman spectrum of the $NaNO_3$ crystal should exhibit two low-frequency lines at 190 and 87 which may be termed the lattice lines. This is confirmed by experiment and two lines having frequency shifts of 185 and 94 at the room temperature have actually been recorded in its Raman spectrum.

Similarly the infra-red spectrum should contain five different frequency shifts. Three for one orientation and two for another with values in qualitative agreement with those calculated have actually been observed in the infra-red absorption. It may, however, be remarked that the force-system postulated cannot be too much relied upon as it is only tentative and is capable of variation. The figures, nevertheless, represent correctly the order of magnitude.

6. *Summary*

By adopting a set of seven constants, four of which pertain to the forces in the free ion and the remaining three to the inter-ionic forces in the crystal, the observed Raman and infra-red spectra of $NaNO_3$ crystal have been satisfactorily explained.

The author wishes to record here his grateful thanks to Prof. S. Bhagavantam for his helpful guidance during the progress of this work.

AN ELECTRICAL METHOD OF STUDYING THE MOVEMENT OF WATER AND SALTS IN SOIL

Part I. A Sensitive A. C. Bridge with an Electronic Null-Point Indicator

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Received January 10, 1944
(Communicated by Dr. L. A. Ramdas)

1. Introduction

The A. C. bridge method, first used by Kohlrausch for measuring the electrical conductivity of solutions, has been employed with numerous modifications by several workers in soil physics[1,2,3] for measuring the electrical conductivity of soils and soil extracts. In the original method of Kohlrausch a buzzer provided the alternating e.m.f. for the bridge and a telephone was used for detecting the null-point. Later workers have introduced modifications and refinements to reduce the errors produced by any lack of balance of out of phase voltages and to obtain a silent null-point.

The difficulties due to phase-angle differences, which in resistance bridges are due mainly to stray capacities in the connecting wires, the electrode system and the balancing resistances, have been overcome by first balancing out these out-of-phase components with a variable capacity connected across the adjustable arm of the bridge. The problem of obtaining a sharp and silent null-point has been only partially solved by making use of thermionic amplification and in some cases, where the telephone is directly connected to the bridge, by making use of grounding circuits[1] for maintaining the telephone circuit at zero potential throughout each cycle of the A. C.

All these methods developed by earlier workers are satisfactory only if the resistances to be measured are fairly low and a very high degree of precision is not aimed at, but if accurate and quick measurments of very high and rapidly changing resistances are to be made these methods have certain limitations.

In the present paper is described an electronic apparatus which has been designed for measuring the rapidly changing resistance of a soil column

between two grid electrodes when water is allowed to rise in the soil column by capillary action. The method described here was found to be quick and accurate and was successfully used in investigating the structure of the water front in an ascending column of moisture in soil, the adsorption of water vapour by air-dry soil and the movement of salts associated with the movement of water in soil. The results of this investigation will be described in the second part of this series.

2. *Disadvantages of the Telephone as a Null-Point Indicator*

Although the telephone, when used in conjunction with an amplifier, is quite satisfactory for the measurement of low resistances, it has certain limitations if the resistances to be measured are very high and a high degree of precision is desired. The main disadvantages of the telephone as null-point indicator are as follows:—

(*i*) *Background noise*:—If an amplifier with a high voltage gain is used in conjunction with a telephone, there is always a certain amount of direct pick up from the source of alternating e.m.f. for the bridge which after amplification appears as a constant background noise. This makes it difficult to fix the exact position of the null-point on the sale of the bridge Electro-static shielding is impracticable as it would be very dificult to shield adequately the input circuit of the amplifier from the wires feeding the alternating e.m.f. and other parts of the bridge.

(*ii*) *Logarithmic response of the human ear*:—This is another factor which introduces a certain amount of uncertainty in finding the exact position of the null-point. The insensitivity of the ear to changes in sound level of less than 2 or 3 decibels is responsible for the apparent flatness of the null-point. This defect is especially marked if the resistances to be measured are of the order of megohms.

(*iii*) *Limited range of frequencies that can be used*:—When the telephone is used the frequency of the applied e.m.f. must necessarily lie within a limited portion of the audible range, *i.e.*, from about 50 to about 8,000 cycles per second. In addition, the response of the ordinary diaphragm type of telephone is not linear but has got a peak in the region of 1000–1500 c/s, and therefore it can be used successfully only within the above narrow band of frequencies.

(*iv*) *The telephone is not phase-selective*, thus its use necessitates a separate balancing of out-of-phase e.m.f's.

To overcome these difficulties it was decided to use some type of visual balance indicator.

3. *Visual Balance Indicators in A.C. Bridges*

Visual balance indicators in A.C. bridges may be classified under the following two main heads: (*i*) those using Meters, and (*ii*) those using Electronic devices.

(*i*) *Meters*:—For the detection of the conditions of balance, using a meter, the output of the bridge is either directly fed to a suitable type of a.c. galvanometer (vibration type, etc.) or it is first rectified by thermionic or copper oxide rectifiers and then fed to an ordinary galvanometer or a sensitive micro-ammeter.

(*ii*) *Electronic devices*:—Under this head come the numerous developments of the cathode-ray tube and also the electron-ray indicator tubes commonly used in radio receivers as tuning indicators.

As the apparatus making use of sensitive meters require frequent and critical adjustments and as our purpose was to develop an instrument which would be sensitive as well as robust and suitable for use under actual field conditions, the use of a meter was ruled out.

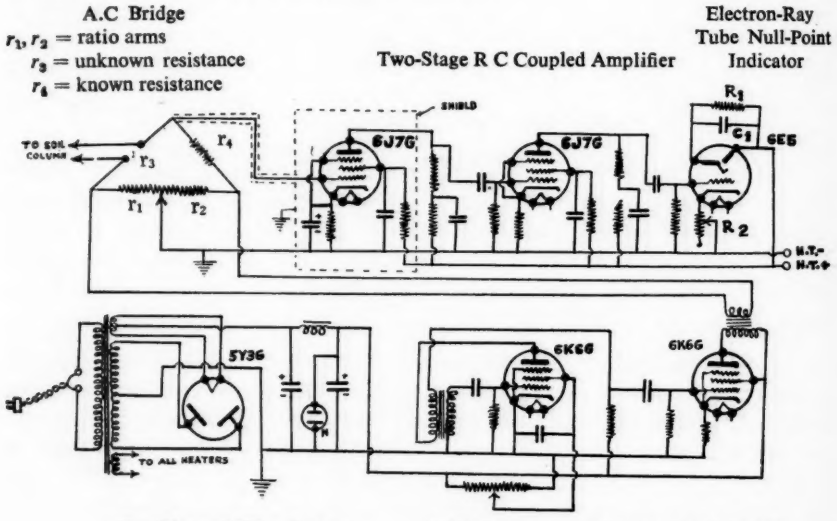

FIG. 1. Schematic circuit diagram of electron-ray tube null-point indicator for A.C. Bridge

The cathode-ray tube, although superior in many ways to all other types of indicators, was not suitable for our purpose as its operating voltages are very high and not easily obtainable under field conditions. It was therefore

decided to use an electron-ray tube which appeared to be the most suitable and promising from the point of view of portability, robustness and also sensitivity. This tube worked satisfactorily on voltages as low as 70 or 80 volts on the target. In addition, it had one useful feature which permitted the compensation for any direct pick-up or lack of balance due to out-of-phase voltages, by suitably adjusting the negative grid bias on the tube.

4. The Electron-Ray Tube

The idea of using the electron-ray tube as a detector of balance in A.C. bridges is not new. It appears to have been first suggested by Ulrey.[4] Later Breazeale, Garman and Koelher have described[5, 6, 7] various arrangements suitable for different types of measurements. The apparatus designed by the present writer which is described in the following pages incorporates some of the desirable features of the apparatus designed by the above authors, with some new modifications to suit the present investigation. A schematic circuit diagram of the complete apparatus including the oscillator, rectifier and filter system is given in Fig. 1.

A type 6 E 5 electron-ray indicator tube has been used for the detection of the condition of balance in this apparatus. This tube has an indirectly heated cathode and the emission is focussed in the form of a beam on a fluorescent target which is maintained at a high positive potential. It has also an anode and two grids, one of which functions as a normal control grid in a triode and controls the anode current of the tube, and the other which is connected to the anode inside the tube and is directly in the path of the electron beam, is known as the ray-control grid. This ray-control grid casts a fan-shaped shadow on the fluorescent target and the angular width of this shadow is determined by the potential difference between the ray-control grid and the target, which is obtained by the flow of the anode current across a high resistance, R_1, connected between the anode and the target. The anode current is, of course, dependent on the negative bias on the control grid. Thus, by changing the value of this negative bias on the tube it is possible to change the angular width of the shadow on the target, the variation in the grid voltage for changing the shadow angle from 100° to 0° being about 3 or 4 volts. The anode current is almost cut off by a grid bias of about 4 volts and therefore there is no appreciable potential difference between the anode (to which is connected the shadow-forming grid) and the target. The electrons, therefore, take a straight path to the fluorescent target casting a fine crack-like shadow of the ray-control grid. Now if this bias on the control grid is made less negative by some means the anode current increases producing a potential difference across the load resistance,

R_1, connected between the anode and the target. Since the shadow-forming grid is now at a negative potential with respect to the target, the electron beam is repelled by its field and the shadow opens out reaching a maximum angular width of 100° when the bias is O volts or slightly positive.

In the present apparatus this bias is obtained by rectifying and suitably filtering the amplified output of the A.C. bridge. The process of rectification is, however, performed in the electron-ray tube itself by the well-known anode-bend method which is usually employed in wireless receivers for demodulating the radio frequency signal. We need not go into the details of the rectifying action of this method as it is treated in great detail in many text-books on wireless communication. The circuit is arranged in such a way that an increase in the A.C. signal input to the grid of the 6 E 5 tube makes the bias less negative, thus increasing the anode current of the tube which consequently results in the opening of the shadow. Now if the A.C. bridge is adjusted to a condition of balance, the A.C. output should be a minimum; therefore, there is little decrease in the negative bias of the 6 E 5 tube and the anode current being almost negligible the angle of the shadow on the target is also a minimum. By suitably adjusting a variable resistance, R_2, in the cathode circuit it is possible to adjust the bias in such a way that when the bridge is correctly balanced the shadow will close down to a fine crack. Any movement of the slider contact of the bridge away from the null-point tends to open the shadow. With a two-stage high gain thermionic amplifier behind the **6 E 5,** a movement of the slider as small as 1 millimetre away from the null-point can easily be detected. This means that a change of resistance of one part in a thousand can easily be detected by this instrument.

5. The Amplifier

As the successful operation and sensitivity of this null-point indicator greatly depend on the gain and stability of the amplifier which precedes it, care has been taken in designing the amplifier to ensure that the requisite sensitivity consistent with stability was obtained. The amplifier makes use of two type 6 J 7 pentodes with resistance capacity coupling in both the stages. By omitting the cathode by-pass condensers in the second valve and the 6 E 5 tube, a certain amount of degeneration is introduced into the circuit which not only increases its stability but also reduces distortion of the signal by making the response more linear. Special care has also been taken to provide adequate interstage shielding to reduce the tendency to oscillate which is common to all amplifiers with high voltage gain. The total gain of

this particular amplifier has not been measured, but by making use of the equation

$$\text{Voltage gain} = \frac{\mu R_L}{R_P + R_L}$$

where μ = amplification factor of the valve
R_L = load resistance, and
R_P = anode-slope resistance of the valve;

it works out to be about 5,000 which appears to be reasonable and consistent with the sensitivity obtained in the instrument.

6. *The Source of Alternating e.m.f.*

In the early stages of this investigation the 50 c/s A. C. mains were used as the source of alternating e.m.f. for the bridge, an ordinary bell transformer being used for stepping down the mains voltage of 230 to about 6 volts. The results obtained with this arrangement were quite satisfactory, as far as sensitivity was concerned, but later on, it was desired also to study whether the frequency of the alternating e.m.f. applied to the bridge had any effect on the position of the null-point and also to see if any polarisation effects were produced at low frequencies. It was, therefore, decided to build a thermionic audio-frequency oscillator, with the desired frequency range. First a single valve oscillator making use of a type 6K6G power pentode and whose frequency was controlled by varying the screen-grid voltage of the pentode valve was built. Although the desired frequency range was obtained, the results obtained with this oscillator were not quite satisfactory as the output was very low. A power stage using another 6K6G tube was then added and the oscillator was found to give an output of approximately 4·5 watts with 300 volts on the plate and it had a frequency range of 25 to 600 cycles per second. The output was, however, not constant throughout the above range of frequencies, the maximum being somewhere at about 400 c/s. The problem of building an oscillator with a constant output should not be a difficult one, but since the variations in the output with frequency neither changed the position of the null-point appreciably nor greatly affected the sensitivity of the apparatus, no attempt has been made in that direction. The coupling between the oscillator and the bridge was effected by using a step-down transformer of the type commonly used in the output stages of radio receivers for matching the plate impedance of the power valve with that of the speech coil of the loudspeaker. The primary impedance of this transformer was about 6000 ohms and that of the secondary was about 2 ohms which was approximately the same as that of the slide

wire of the bridge. The high tension voltages and the heater current for the oscillator were obtained from a neon-tube stabilised rectifier unit delivering about 130 milliamperes at 350 volts. Since another small high tension unit was available, it was used for the amplifier and the electron-ray tube; but there is no reason why the same power pack should not be used both for the oscillator as well as for the electron-ray tube and amplifier, provided sufficient care is taken to introduce adequate decoupling between the two units.

Making use of the values given by Koehler for R_1 and C_1 it was found that the response of the electron-ray tube became sluggish which was undesirable for our investigation, where very rapidly changing resistances were to be measured. As will be seen from the circuit diagram, R_1 and C_1 form a circuit with a time constant; and with a resistance of 1 megohm and a capacity of $1\mu fd$, this constant will be one second. This means that it will take one second for the shadow to become steady after an adjustment of the slider of the bridge has been made. This was found to be rather slow for our purpose. A value of 300,000 ohms was therefore chosen for R_1 which, with a capacity 1 μfd, was found to have a sufficiently quick response. Any reduction in the value of R_1 will, of course, reduce the sensitivity of the circuit, although it will also make the response of the tube faster. The value of R_1 chosen is therefore a compromise.

7. *Method of Making Measurements*

With the oscillator switched off, *i.e.*, no e.m.f. applied to the bridge, the variable resistance, R_2, in the cathode circuit of the electron-ray tube is adjusted until the shadow just closes. The tube is now operating on the lower bend of the anode current—grid voltage characteristic of the tube and there is no appreciable anode current flowing. If the oscillator is now switched on and the bridge adjusted, it will be found that the shadow again closes when the bridge is exactly balanced. If there is any residual opening of the shadow due to direct pick-up, etc., it may be made to close again by a slight adjustment of R_2.

8. *Conclusion*

The electron-ray tube apparatus described above has been used for measurements of the variations in electrical conductivity of Poona black cotton and the Punjab 'normal' soils with approaching moisture from below. It has also been used for studying the adsorption of water vapour by air-dry and heated Poona black cotton soil exposed to saturated air. The results of this investigation will be described in Part II of this paper. The

apparatus is also being used in other investigations where the measurement of electrical conductivity is involved, *viz.*, in studying the effect of transpiration on the electrical conductivity of the sap in growing plants and plant cuttings.

The following features of the present apparatus may be regarded as improvements on the arrangements used by previous workers:

(*i*) The response of the apparatus is much faster than of that described by Koehler.

(*ii*) The present apparatus makes use of a high gain amplifier, which has been stabilised by introducing degeneration into the circuit. Consequently a higher sensitivity has been obtained without sacrificing stability which does not appear to have been done in the previous instruments.

(*iii*) The earthing and shielding arrangement in the circuit makes it non-susceptible to outside electrical disturbances. This is difficult with Garman's apparatus where a direct coupled amplifier is used.

(*iv*) The apparatus makes use of an audio-farquency power oscillator with variable frequency.

In conclusion, the writer wishes to express his gratitude to Dr. L. A. Ramdas, Agricultural Meteorologist, for suggesting the problem, for guidance and encouragement during the course of the investigation and for providing the necessary facilities for the work.

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SCATTERING OF LIGHT IN SINGLE CRYSTALS

Intensity Measurements

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1. Introduction

EXPERIMENTAL observations regarding the relative intensities of the Rayleigh and Raman scattering in gases have so far been very meagre. Bhagavantam[1] showed that the intensity of the Rayleigh line in most typical gases is a few thousand times that of the vibrational Raman line. The cases of hydrogen and deuterium constitute an exception as the exciting line in them is only a few hundred times stronger than the Raman line. On the other hand, several authors[2–6] have determined the ratio of the intensity of the Rayleigh line to that of some of the prominent Raman lines in liquids like benzene, carbon tetrachloride, chloroform, etc. The results obtained by them differ to some extent amongst themselves but the general conclusion that the intensity of the Rayleigh line in liquids is a few hundred times that of the Raman lines is confirmed by all the workers. No work has at all been done so far in this direction with crystals. It will be of great interest to know the ratio of intensity of Rayleigh to that of the Raman scattering in the case of solids because such results can confidently be expected to throw light on the fundamental problem regarding the nature of the Raman scattering in solids. There are several experimental difficulties in the way of obtaining accurate results but an attempt is now made to develop a suitable technique for solving the problem.

Two typical crystals, calcite and quartz, which are available in this laboratory in the form of perfectly transparent and flawless one inch cubes with all their faces polished have been used in the present investigation. The results obtained are of great interest and are accordingly reported in this paper.

2. Experimental Details and Results

It is difficult to obtain the ratio of the relative intensities of Rayleigh and Raman scattering in crystals directly by photographic methods, because with the Rayleigh scattering is usually mixed up a large amount of spurious or parasitic light. As such, a special method has been adopted here to obtain an estimate of this ratio. This will be clear from Tables I and II.

The Raman spectra of the crystal (one inch cube) and a chosen liquid* contained in a glass cell of exactly the same dimensions as the crystal are obtained under identical conditions on the same plate. Great care has been taken to see that the time of exposure, the intensity of the lamp and conditions of illumination remained the same in both cases. A set of intensity marks is given on each plate by the method of varying slit widths using a quartz globe tungsten ribbon lamp as the source. The intensities of the 1085 line in calcite and of the 465 line in quartz are compared in turn with that of the 460 line in carbon tetrachloride. The results obtained are given in column 4 of each of the tables given below.

TABLE I. *Calcite*

Optic axis parallel to	$\frac{\text{I Rayleigh (liquid)}}{\text{I Rayleigh (crystal)}}$	$\frac{\text{I Rayleigh (liquid)}}{\text{I Raman (liquid)}}$	$\frac{\text{I Raman (crystal)}}{\text{I Raman (liquid)}}$	$\frac{\text{I Rayleigh (crystal)}}{\text{I Raman (crystal)}}$
OX	73	400	1·45	3·8
OY	83		2·20	2·2
OZ	65		0·87	7·1

TABLE II. *Quartz*

Optic axis parallel to	$\frac{\text{I Rayleigh (liquid)}}{\text{I Rayleigh (crystal)}}$	$\frac{\text{I Rayleigh (liquid)}}{\text{I Raman (liquid)}}$	$\frac{\text{I Raman (crystal)}}{\text{I Raman (liquid)}}$	$\frac{\text{I Rayleigh (crystal)}}{\text{I Raman (crystal)}}$
OX	77	400	0·96	5·4
OY	93		1·22	3·5
OZ	103		0·55	7·1

OX, OY and OZ represent respectively the direction of incidence, of scattering and the vertical. In column 2 of each of the tables are given figures obtained by Bhagavantam and Narayana when they compared the intensities of Rayleigh scattering in calcite and quartz with that in air by employing intermediate liquid standards. These figures may be seen to agree with those given in their paper already referred to if the conversion factor I Rayleigh (liquid CCl_4)/I Rayleigh (air) = 918 adopted by them is taken into account. In column 3 of each of the tables is given the ratio of the Rayleigh line to that of the 460 Raman line in CCl_4 as determined by Veerabhadra Rao in this laboratory. It is easily seen that the figure given in the last column is obtained by dividing 400 with the product of coulmns 2 and 4 in each case and this represents the desired ratio.

* In this paper, results obtained when the chosen liquid is carbon tetrachloride only are given. Benzene as a standard has also been experimented upon but the results are more difficult to interpret because of the large rotational wing that accompanies the Rayleigh scattering. This complication is practically absent in carbon tetrachloride.

3. *Discussion of Results*

The ratio of the intensities of Rayleigh and Raman scattering in a gas, a liquid and a crystal for one orientation are given in Table III for comparison.

TABLE III

Substance	Frequency of the Raman line	$\frac{\text{I Rayleigh}}{\text{I Raman}}$
Oxygen	1560	3330
Carbon tetrachloride	460	400
Calcite	1085	3·8

Comparatively low ratios obtained and reported in this paper for calcite and quartz are very significant. Since the intensity of Raman scattering in crystals is found to be of the same order as that observed in liquids, when equal volumes are illuminated by beams of the same intensity, we have to conclude that the Rayleigh scattering, mass per mass, has become very faint in the case of crystals whereas Raman scattering has retained its strength. This suggests that while Rayleigh scattering continues to be coherent, Raman scattering continues to be incoherent. The exact significance of such statements in relation to the mechanism of scattering in crystals is not clear and a discussion of the same will not be attempted now. The state of polarisation of the aggregate scattered light in crystals obtained by visual determinations cannot be taken as representing the character of Rayleigh scattering even approximately. Such results will be greatly influenced by the presence of depolarised Raman scattering because in the case of crystals the latter, if present, has an intensity comparable to that of the Rayleigh scattering. Only a spectroscopic investigation can lead to reliable values.

4. *Summary*

Employing carbon tetrachloride as an intermediate standard, the relative intensities of Rayleigh and Raman lines in specially cut crystals of calcite and quartz have been determined for different orientations. The Rayleigh line, in different instances, is found to possess an intensity which is only about two to seven times that of the principal Raman line.

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EFFECT OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES

Part III. Liquids

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(Communicated by Prof. S. Bhagavantam)

Placzek's theory indicates that both the Stokes and the anti-Stokes Raman lines should increase in intensity with increase of temperature. The expressions for the intensities of the Stokes and the anti-Stokes lines as a function of temperature are given by (1) and (2).

$$I_{(\nu-\nu_j)} \propto (\nu-\nu_j)^4 \frac{1}{1-e^{-\frac{h\nu_j}{KT}}} \qquad (1) \qquad I_{(\nu+\nu_j)} \propto (\nu+\nu_j)^4 \frac{1}{e^{\frac{h\nu_j}{KT}}-1} \qquad (2)$$

Not much work has been done as regards the effect of temperature on the intensities of the Raman lines either in solids or in liquids. The early work of Landsberg and Mandelstamm[1] in the case of quartz, shows that the intensity of Stokes lines increases with temperature while the more recent work of Ornstein and Went[2] in the case of calcite and quartz, on the other hand, shows a marked decrease of intensity with increase of temperature. In two previous communications,[3,4] the author has published some results in the case of a few typical crystals. The following are the main features observed by the author in the cases he has studied. The Stokes lines decrease in intensity with increase of temperature. The anti-Stokes lines generally increase in intensity with increase of temperature but not to the expected extent. The ratio of the intensities of the Stokes and the anti-Stokes lines in all cases is in conformity with the theoretically expected results. Some special features observed in the case of calcite are that the low frequency lines decrease in intensity more rapidly than the others and that the anti-Stokes lines show slight decrease in intensity. Small shifts of the low frequency lines towards the exciting line have also been noticed.

As regards liquids, Krishnan[5] pointed out that in the Raman spectrum of liquid carbon tetrachloride, the Stokes lines become weaker and the anti-Stokes lines stronger in intensity with increase of temperature. Ananthakrishnan[6,7] concluded from the spectrograms he has obtained in the case of liquid CCl_4 over an interval of temperature extending from 25° C. to 200° C. that the integrated intensities of the Stokes lines do not increase with increasing temperature and also that the anti-Stokes lines increase in intensity but not to such an extent as is required by Placzek's theory.

The work so far done in the case of liquids is very meagre and purely qualitative. As such and to fall in a line with the previous work done by

the author in the solids, the present investigation regarding the effect of temperature on the intensities of Raman lines in some typical liquids like carbon tetrachloride, benzene, chlorobenzene, etc., has been taken up.

2. *Experimental*

The experimental arrangements are the same as those described by the author in the previous communications. Light from a 6-inch quartz mercury arc lamp condensed by an 8-inch condenser is allowed to fall on the slit of the Raman tube containing the liquid under investigation. The scattered light coming out from the window of the tube is focussed on to the slit of a Fuess spectrograph. The Raman tube containing the liquid is heated by a specially made electric heater and a thermometer placed in contact with the tube indicated the temperature with an accuracy of $\pm 2^{\circ}$ C. Intense and clear spectrograms are obtained in a very short time. The intensity of the source and the time of exposure are kept constant while obtaining the spectra at different temperatures. The Raman spectra at various temperatures along with a set of intensity marks given by the method of varying slit widths using the standard quartz globe tungsten ribbon lamp as the source are recorded on the same plate. The intensities of the various lines are computed in the usual way. As the lines did not show any appreciable broadening in the temperature region studied, only peak intensities have been compared.

3. *Results and Discussion*

Tables I, II, III and IV contain the results regarding the effect of temperature on the intensities of the Stokes Raman lines in liquid carbon tetrachloride, benzene, normal butyl alcohol and chlorobenzene respectively.

TABLE I. *Carbon Tetrachloride*

Frequency $cm.^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
215	305	1·00	1·00	1·00
	340	1·05	1·07	1·02
315	305	1·00	1·00	1·00
	340	0·94	1·05	1·12
460	305	1·00	1·00	1·00
	340	0·90	1·04	1·16
760	305	1·00	1·00	1·00
	340	0·84	1·01	1·20
790	305	1·00	1·00	1·00
	340	0·84	1·01	1·20

TABLE II. *Benzene*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
605	305	1·00	1·00	1·00
	345	0·89	1·03	1·16
850	305	1·00	1·00	1·00
	345	0·93	1·01	1·09
990	305	1·00	1·00	1·00
	345	0·97	1·01	1·04
1180	305	1·00	1·00	1·00
	345	0·90	1·01	1·12
1585	305	1·00	1·00	1·00
	345	0·89	1·00	1·12
1605	305	1·00	1·00	1·00
	345	0·91	1·00	1·10
3055	305	1·00	1·00	1·00
	345	0·97	1·00	1·03

TABLE III. *Normal Butyl Alcohol*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
825	305	1·00	1·00	1·00
	373	0·60	1·02	1·70
960	305	1·00	1·00	1·00
	373	0·72	1·02	1·42
1300	305	1·00	1·00	1·00
	373	0·76	1·01	1·33
1450	305	1·00	1·00	1·00
	373	0·75	1·00	1·33
2865	305	1·00	1·00	1·00
	373	0·76	1·00	1·32
2910	305	1·00	1·00	1·00
	373	0·80	1·00	1·25
2935	305	1·00	1·00	1·00
	373	0·82	1·00	1·22
2960	305	1·00	1·00	1·00
	373	0·82	1·00	1·22

TABLE IV. *Chlorobenzene*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
200	305	1·00	1·00	1·00
	358	0·88	1·10	1·25
	395	0·73	1·18	1·62
420	305	1·00	1·00	1·00
	358	0·87	1·06	1·22
	395	0·74	1·10	1·49
700	305	1·00	1·00	1·00
	358	0·92	1·02	1·11
	395	0·85	1·05	1·24
1000	305	1·00	1·00	1·00
	358	0·90	1·01	1·12
	395	0·78	1·02	1·31
1020	305	1·00	1·00	1·00
	358	0·91	1·01	1·11
	395	0·82	1·02	1·24
1080	305	1·00	1·00	1·00
	358	0·88	1·01	1·15
	395	0·75	1·02	1·36
1580	305	1·00	1·00	1·00
	358	0·92	1·00	1·09
	395	0·85	1·00	1·18
3065	305	1·00	1·00	1·00
	358	0·87	1·00	1·15
	395	0·73	1·00	1·37

Tables V and VI contain the results regarding the effect of temperature on the intensities of the anti-Stokes Raman lines in carbon tetrachloride and chlorobenzene respectively.

TABLE V. *Carbon Tetrachloride*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
−215	305	1·00	1·00	1·00
	340	1·12	1·19	1·06
−315	305	1·00	1·00	1·00
	340	1·18	1·24	1·05
−460	305	1·00	1·00	1·00
	340	1·22	1·31	1·07

TABLE VI. *Chlorobenzene*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
−200	305	1·00	1·00	1·00
	358	1·18	1·27	1·08
	395	1·25	1·45	1·16

Tables VII and VIII contain results regarding the effect of temperature on the ratio of the intensities of the Stokes and the anti-Stokes Raman lines in carbon tetrachloride and chlorobenzene respectively.

TABLE VII. *Carbon Tetrachloride*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{h\nu_j}{e^{kT}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 \cdot \frac{h\nu_j}{e^{kT}}$	$\frac{I_S}{I_{AS}}$ obs.
215	305	2·75	2·55	2·50
	340	2·48	2·30	2·34
315	305	4·40	3·95	4·08
	340	3·78	3·39	3·26
460	305	8·71	7·41	7·52
	340	6·97	5·93	5·60

TABLE VIII. *Chlorobenzene*

Frequency cm.$^{-1}$	Temperature °K.	$\frac{h\nu_j}{e^{kT}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 \cdot \frac{h\nu_j}{e^{kT}}$	$\frac{I_S}{I_{AS}}$ obs.
200	305	2·56	2·39	2·53
	358	2·23	2·08	1·89
	395	2·07	1·93	1·48

From the results given above, the following conclusions may be drawn:—

(1) The Stokes lines decrease in intensity with increase of temperature excepting the line at 215 cm.$^{-1}$ in CCl_4.

(2) The anti-Stokes lines increase in intensity with increase of temperature but not to the expected extent.

(3) The ratio of the intensities of the Stokes and the anti-Stokes lines at various temperatures is in good agreement with the expected results.

In liquids, the large expansion at high temperatures causes a diminution in the density of the scattering medium and to that extent there will be a decrease in the number of effective scattering centres per unit volume. The effect of taking density into consideration is to increase the observed intensities of the Stokes lines. But in the cases studied in the present paper it can easily be seen that the intensities even after applying the correction for density, taking that the number of effective scattering centres per unit volume is inversely proportional to the density, are not equal to the calculated values.

A detailed explanation of the results obtained by the author both in solids and liquids will be dealt with in a separate communication.

4. *Summary*

The effect of temperature on the intensities of the Raman lines in some typical liquids like carbon tetrachloride, benzene, normal butyl alcohol and chlorobenzene has been studied. It has been found that the Stokes lines in all the cases studied, excepting the line at 215 cm.$^{-1}$ in CCl_4, decrease in intensity with increase of temperature whereas the anti-Stokes lines increase in intensity but not to the expected extent. The ratio of the intensities of the Stokes and anti-Stokes lines, however, is in good agreement with the calculated value. The intensities of the Stokes lines, even after applying the correction for the change in density on the assumption that the number of effective scattering centres will be inversely proportional to the density, are not equal to the calculated values.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam, HON.D.SC., for his kind interest in the work.

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THE *NEW LIGHT-EFFECT* IN CHLORINE UNDER ELECTRICAL DISCHARGE

Part I. Influence of Different Irradiations on the Production of the Phenomenon under Constant Electrical Conditions

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(Communicated by Prof. S. S. Joshi, D.Sc., F.A.Sc.)

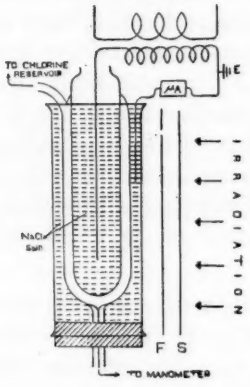
That the *new light-effect*[1,2,3] is markedly sensitive to but small variations in the magnitude of the numerous factors characteristic of an electrical discharge has been emphasized previously.[4,5,6,8] In the work now to be reported, as far as practicable, all these factors, such as the gas pressure (11 cm. Hg), applied potential (about 9400 volts r.m.s.), the temperature (23° C.), the frequency of the A.C. supply (50 cycles per second), '*ageing*' of the system under the discharge, etc., have been kept constant. The only principal factor which has been allowed to vary is the nature of the light-source. These results (which are essentially an extension of earlier, preliminary ones,[2,3,8] were possible due to the loan of a Cambridge A.C. microammeter) reveal a new type of a *light-effect*, in which i the current produced under an electrical discharge in chlorine and other gases, is *diminished* on exposure to light. This diminution is instantaneous and also reversible, *i.e.*, i under light is restored fully to the initial value on shutting off the light.[5]

The electrical discharge was produced in the annular space of a Siemens' type, soft glass ozoniser A (Fig. 1) filled at 11 cm. pressure with chlorine which was purified over liquid air. The ozoniser terminals, represented by a moderately concentrated saline solution inside the inner tube and in the bath surrounding the outer tube of the ozoniser, were connected to the secondaries of a high tension transformer. Its voltage was kept constant at the above-mentioned value by hand regulation of a variable rheostat introduced in the primary of the transformer. The discharge current i flowing through the ozoniser at the above potential was observed with an A.C. microammeter (μA in Fig. 1) connected between the earth and one of the ozoniser terminals. The microammeter was shunted with a *non-inductive* resistance varied in the range 100 to 700 ohms.

Five principal series of experiments were carried out using (*a*) 200 watt, 220 volt incandescent bulb, (*b*) copper arc, (*c*) iron arc, (*d*) carbon arc and (*e*) mercury vapour lamp. Employing each of these light-sources, four sets of observations were carried out for the *light-effect, i.e.*, the diminution of i produced, when (i) the ozoniser was irradiated directly, and when each of *a*, *b*, *c*, *d* and *e* was screened successively with (ii) the red, (iii) green and (iv) violet filters kept at F in Fig. 1. For this purpose, long strips of carefully selected coloured glass were employed. The transmission-limits of each of the filters were observed with a Hilger's constant deviation glass spectrograph (Table I).

The ozoniser A was enclosed in an opaque box with a window in one side which could be closed with the desired light-filter, F. A shutter (S, in Fig. 1) next to the light-filter and worked by a pulley arrangement allowed light from any of the sources, to irradiate the ozoniser after passing through the filter F. The current in the dark was measured *with the light-source on,*

FIG. 1 (OZONISER A)
EFFECT OF LIGHT ON ELECTRICAL DISCHARGE IN CHLORINE



and the shutter S in position, so as to cover the filter F (Fig. 1); on moving the shutter, the ozoniser current diminished immediately due to light. These results are shown in Table I, in four vertical columns. Thus, for example, using (unfiltered) white light from the 200 watt incandescent bulb, results under the first column show the microammeter readings taken with a series of shunt resistances for i the current in the dark; the corresponding values on irradiation are shown in the next column. The difference is a measure of Δi the *light-effect*; this diminution is shown in the next column as a percentage of i the original current, in dark. These results show clearly

TABLE I (OZONISER A)

Light-Effect under different kinds of Irradiation

Primary potential .. .. .. 35 volts (r.m.s.)
„ current .. .. .. About 0·25 amp.
Frequency of the A.C. supply .. „ 50 cycles/sec.
Transformer ratio 267
Secondary potential .. .. About 9400 volts (r.m.s.)
Ozoniser A, PCl_2 .. .. „ 11 cm.Hg (28 C.)

Microammeter shunt	Filters															
	(i) White (7800–3700 Å)				(ii) Red (7070–6070 Å)				(iii) Green (5775–5070 Å)				(iv) Violet (4750–4000 Å)			
	i				*i*				*i*				*i*			
	In dark	In light	Δ *i*	Photo diminution %	In dark	In light	Δ *i*	Photo diminution %	In dark	In light	Δ *i*	Photo diminution %	In dark	In light	Δ *i*	Photo diminution %
	(*a*) *Source of Irradiation*: 200 *watt bulb*															
100	21	14	7	33	21·5	21	0·5	2	21·5	21	0·5	2	21	16	5	24
200	30	23	7	23	33	32·5	0·5	2	32	31·5	0·5	2	32	26	6	19
300	41	32	9	22	44	43	1	3	41	40·5	0·5	1	42	35	7	17
400	53	43	10	19	55	54	1	2	53	52·5	0·5	1	54	46	8	15
500	66	46·5	9·5	14	67	66	1	2	66	65	1	2	67	58	9	13
600	79	69·5	9·5	12	81	80	1	1	81	80	1	1	79	71	8	10
700	91	81·5	9·5	10	93	92	1	1	93	92	1	1	92	85	7	8
	(*b*) *Source of Irradiation*: *Copper arc*															
100	22	17	5	22	22·5	22·5	0	0	22	21·5	0·5	2	21	18	3	14
200	32	26	6	19	33	33	0	0	32	31·5	0·5	1	31	27	4	13
300	42	34	8	19	43·5	43·5	0	0	43	42·5	0·5	1	42	35	5	12
400	53	54	9	17	55	55	0	0	54	53·5	0·5	1	54	47·5	6·5	12
500	66	57	9	14	67·5	67·5	0	0	66	65·5	0·5	1	67	70	7	11
600	80	70·5	9·5	11	80	80	0	0	78	77·5	0·5	1	80	73	7	9
700	91	82	9	10	91	91	0	0	91	90·5	0·5	1	92	84	8	9

TABLE—I (*Contd*).

Microammeters shunt	Filters															
	(i) White (7800-3700 Å)				(ii) Red (7070-6070 Å)				(iii) Green (5775-5070 Å)				(iv) Violet (4750-4000 Å)			
	i			Photo diminution %	*i*			Photo diminution %	*i*			Photo diminution %	*i*			Photo diminution %
	In dark	In light	Δ *i*		In dark	In light	Δ *i*		In dark	In light	Δ		In dark	In light	Δ *i*	
	(c) *Source of Irradiation : Iron arc*															
100	21	9	12	57	20	20	0	0	20	19·5	0·5	3	21	10	11	52
200	32	18	14	44	30·5	30	0·5	2	31	30·5	0·5	2	32	19	13	41
300	42	24	18	43	41·5	41	0·5	1	41	40	1	2	43	26	17	50
400	54	34	20	37	54	53·5	0·5	1	53	52	1	2	55	35	20	36
500	66	44	22	33	66	65	1	2	66	64·5	1·5	2	68	46	22	32
600	79	57	22	28	79	78·5	0·5	1	80·5	79·5	1	2	81	59	22	27
700	90	68	22	24	91	90	1	1	92	91	1	1	93	72	21	23
	(d) *Source of Irradiation : Carbon arc*															
100	21	10	11	52	20	19·5	0·5	3	20	19·5	0·5	2	20	10	10	50
200	31	18	33	42	30·5	30·0	0·5	2	30·5	29·5	0·5	2	31	20	11	36
300	41	26	15	37	41	40·5	0·5	1	42	41·5	0·5	1	41	27	14	34
400	53	33	20	38	53	52	1	2	54	53	1	2	53	32	21	40
500	66	45	21	32	56	64·5	1·5	2	66	65	1	2	66	47	19	29
600	79	58	21	27	79	77·5	1·5	2	79	78	1	1	80	60	20	25
700	91	72	19	21	91	90	1	1	91	90	1	1	92	75	17	19
	(e) *Source of Irradiation : Mercury vapour lamp*															
100	21	10	11	52	21	21	0	0	21	20·5	0·5	2	21	12·5	8·5	41
200	30·5	19	11·5	38	31·5	31·5	0	0	32·5	32	0·5	2	31	21	10	32
300	42	27	15	36	42	42	0	0	42·5	41·5	1	2	41	28·5	12·5	31
400	55	37	18	33	54	54	0	0	55	54	1	2	53	37·5	15·5	29
500	67	49	18	27	67	67	0	0	68	67	1	1	67	62	15	22
600	80	62	18	23	80	80	0	0	81	80	1	1	80	65	15	19
700	92	75	17	19	92	92	0	0	92	91	1	1	92	77	14	15

the general occurrence of the new effect, namely a photo-reduction of the conductivity under electrical discharge, a possibility which has been hitherto practically ignored in the now extensive literature on the electrical discharge phenomenon. The effect is seen to be as high as about 33%, 22%, 57%, 52% and 52% on direct irradiation from an incandescent bulb, copper arc, iron arc, carbon arc and mercury vapour lamp respectively. The interposition of a violet filter reduces the *light-effect* in all cases, to a value which at its maximum varies in the range 45 to 52%. The substitution of the green and red filters reduces markedly the corresponding *light-effect*. These results suggest that the effect varies in the order, white > violet > green, red.[5,6,7,8] The light-intensity is also a determining factor.[5,6,7,8] The much greater effect both under direct and violet filtered radiations, using both an iron arc and mercury vapour lamp, compared with that due to a 200 watt bulb is to be attributed to the fact that the short wave region is more intense in the former than in the latter.[6,7,8] An examination of the light intensities for *a*, *b*, *c*, *d* and *e* using the above filters with a P/1200 Kodak, super-panchromatic plate, a photoelectric cell and a thermopile has shown that the above quantity was lowest in green, the relative order being white (*i.e.*, unfiltered) > red > violet > green. That Δi the *light-effect* under green should be more than comparable with that due to red (Table I), despite the greater intensity available in the latter shows that intensity is the less predominant factor than frequency in determining the magnitude of this phenomenon, a deduction made previously from independent data.[5,6,7,8] In agreement with earlier results it is also seen that the *light-effect* under the direct (that is, unfiltered) radiations from any of the five light-sources employed is comparable with that due to the filtered violet.[5,6,7,8]

As has been suggested earlier,[6,7,8] a possible explanation of the fact that this *light-effect* is markedly greater under violet than under either green or red may be that the violet lies within the absorption spectrum of chlorine.[9,10] It is necessary, however, to draw attention to the considerations adduced by Joshi suggesting that the phenomenon might occur independently of the 'characteristic' light-absorption of chlorine.[5,11]

It is seen from Table I, say, in the case of *a*, the unfiltered white from the 200 watt bulb, that a change of the shunt resistance from 100 to 700 ohms has increased the microammeter deflection from 21 to 91 units for the discharge current in dark. It is remarkable, however, to see in all the cases that although Δi has increased from 7 to 9·5 units, the corresponding percentage photo-diminution has *decreased* from 33 to 10. Since no change in the main electrical constants of the discharge circuit has

been made with the exception of the microammeter shunt, it is to be anticipated on general grounds that the percentage photo-diminution would be sensibly constant. Work is in progress to investigate in some detail this apparent anomaly, as also the nature of other determinants for the production of this phenomenon.

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Summary

Detailed results are given for the production of a *new light-effect in chlorine.* It is that the conductivity under an electrical discharge is reduced instantaneously and reversibly on irradiation. This effect increases by increasing the frequency and the intensity of light and that the former is the more important factor.

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